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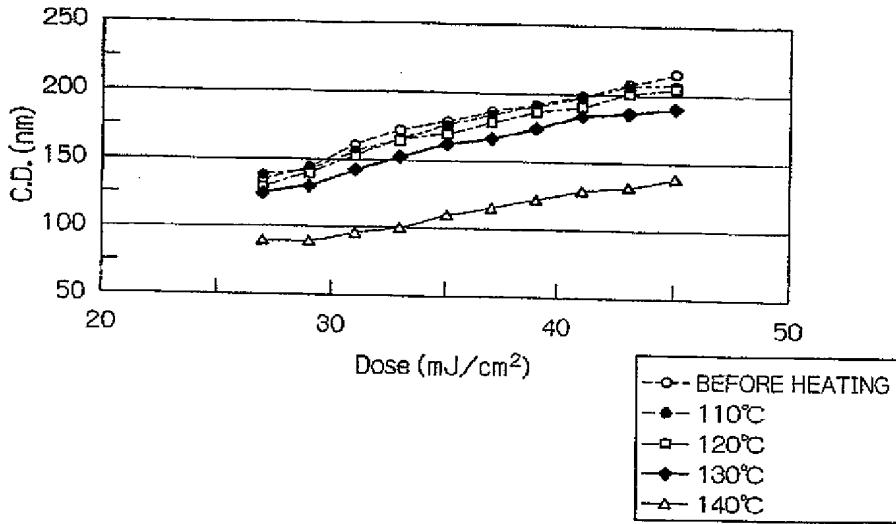
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(54) Title: METHOD OF FORMING RESIST PATTERN, POSITIVE RESIST COMPOSITION, AND LAYERED PRODUCT



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(57) Abstract: There are provided a method of forming a resist pattern that enables the resist pattern to be formed with good control of the pattern size, as well as a positive resist composition used in the method, and a layered product formed using the positive resist composition. In the above method a positive resist composition comprising a resin component (A), which contains a structural unit (a1) derived from a (meth)acrylate ester represented by a general formula (I) shown below, and displays increased alkali solubility under action of acid, and an acid generator component (B) that generates acid on exposure is applied to a substrate, a prebake is conducted, the resist composition is selectively exposed, post exposure baking (PEB) is conducted, alkali developing is then used to form a resist pattern, and the pattern size of the thus produced resist pattern is then narrowed by heat treatment.

DESCRIPTION

METHOD OF FORMING RESIST PATTERN, POSITIVE RESIST COMPOSITION,
AND LAYERED PRODUCT

TECHNICAL FIELD

The present invention relates to a method of forming a resist pattern, comprising a step for narrowing the pattern size of the resist pattern by conducting a heat treatment following formation of the resist pattern, as well as a positive resist composition that is ideally suited to use within such a method, and a layered product that uses such a positive resist composition.

BACKGROUND ART

In recent years, in the manufacture of semiconductor elements and the like, advances in lithography techniques have lead to rapid progress in the field of miniaturization. Typically these miniaturization techniques involve shortening of the wavelength of the exposure light source. Until recently, ultraviolet radiation such as g-lines and i-lines have been used as the exposure light source, but recently, KrF excimer lasers (248 nm) have been introduced, and even ArF excimer lasers (193 nm) are now starting to be used.

Resists for use with light sources such as KrF excimer lasers and ArF excimer lasers require a high resolution capable of reproducing a pattern of minute dimensions, as well as good sensitivity relative to light sources with this type of short wavelength. One example of a type of known resist that satisfies these conditions is a chemically amplified positive type resist composition comprising a base resin that displays increased alkali

ultra-miniaturization, research is also being conducted on pattern formation methods to develop techniques capable of overcoming the resolution limits of resist materials.

One example of such a technique, which has resulted in a number of different proposals, is a method in which a resist pattern is first formed using photolithography, and subsequent heat treatment is then used to further reduce the size of the resist pattern.

For example, the patent reference 2 discloses an omission pattern formation method in which an omission pattern is first formed in a pattern formation resist applied to the surface of a substrate, a mixing generation resist that mixes with the pattern formation resist is then applied across the entire surface of the substrate, baking is performed so that a mixed layer is formed on the side walls and the surface of the pattern formation resist, and the unmixed sections of the mixing generation resist are then removed, enabling the pattern size to be reduced by the dimensions of the mixed layer.

Furthermore, the patent reference 3 discloses a pattern formation method in which a resist pattern comprising an acid generator is formed on a substrate, the entire surface of the substrate is coated with a resin that becomes insoluble in the presence of acid, a heat treatment is then conducted, causing acid to diffuse from the resist into the resin, forming a resist layer of uniform thickness at the interface between the resin and the resist pattern, and developing is then used to remove those sections of the resin into which the acid has not diffused, thereby enabling the pattern size to be reduced by the dimension of the aforementioned uniform thickness.

Furthermore, recently, thermal flow processes in which the resist pattern is fluidized through heat treatment or the like, thereby enabling a reduction in the pattern size, have also been proposed. In a thermal flow method, a resist pattern is first formed using photolithography, and by subsequently heating the pattern to a temperature

ArF resist is used, the degree to which the pattern size reduces (the degree of narrowing) differs for differing patterns even on the same substrate, resulting in a problem that resist patterns of different pattern sizes can be formed on a single substrate (namely, variation can develop in the narrowed resist pattern size).

DISCLOSURE OF INVENTION

Accordingly, an object of the present invention is to provide a method of forming a resist pattern comprising a narrowing step for narrowing the pattern size of a resist pattern using the above type of heat treatment, wherein the pattern size following the narrowing process is easily controlled and suffers minimal variation, as well as a positive resist composition used in such a method, and a layered product using such a positive resist composition.

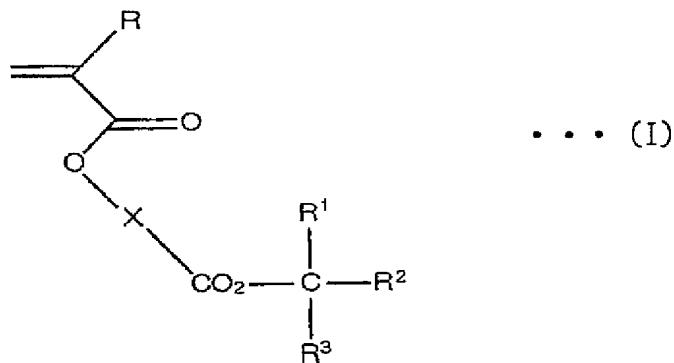
As a result of intensive research, the inventors of the present invention believe that the cause of variations in the pattern size is the fact that the temperature dependency of the fluidity of conventional ArF resists is very high, so that when heating is conducted at a temperature near the softening point of the resist layer, even very minor variations in temperature cause the fluidity to alter, thereby causing the degree to which fluidization occurs to vary depending on the position of the resist pattern, even on a single substrate.

In other words, when heat treatment is conducted on a resist following developing in order to narrow the pattern size, it is essential that a resist pattern of uniform pattern size is formed on a single substrate, so that the hole diameters of the plurality of holes in a hole pattern are uniform, and the space width in a L&S pattern is uniform. In order to achieve this result, the pattern size preferably reduces by a constant quantity (namely, the degree of narrowing is constant) relative to the pattern size following developing (prior to the heat treatment). However, with conventional ArF resists, even very minor variations

ester of a specific structure, a resist pattern could be formed with excellent control of the pattern size, and were hence able to complete the present invention.

In other words, a first aspect of the present invention for resolving the above problems is a method of forming a resist pattern comprising: a resist pattern formation step, in which a positive resist composition comprising a resin component (A) that displays increased alkali solubility under the action of acid, and an acid generator component (B) that generates acid on exposure is applied to a substrate, a prebake is conducted, the resist composition is selectively exposed, post exposure baking (PEB) is conducted, and alkali developing is then used to form a resist pattern; and a narrowing step in which the pattern size of the produced resist pattern is narrowed by heat treatment, wherein

the component (A) utilizes a resin with a structural unit (a1) derived from a (meth)acrylate ester represented by a general formula (I) shown below:



wherein, R represents a hydrogen atom or a methyl group; X represents a hydrocarbon group with 1 to 4 rings; R¹ to R³ either each represent, independently, a lower alkyl group, or alternatively, one of R¹ to R³ represents a lower alkyl group, and the other two groups represent lower alkylene groups, the terminals of which are bonded together to form a single ring containing 5 or 6 carbon atoms including the bonded terminal carbon atoms.

to an example 1 (wherein FIG. 1A shows the results for a dense pattern, and FIG. 1B the results for an isolated pattern).

FIG. 2A and 2B are graphs showing the variation in the hole diameter (C.D.) of a hole pattern relative to the exposure (dose), for both the situation prior to heat treatment, and the situation following heat treatment at a variety of different temperatures according to a comparative example 1 (wherein FIG. 2A shows the results for a dense pattern, and FIG. 2B the results for an isolated pattern).

BEST MODE FOR CARRYING OUT THE INVENTION

As follows is a description of embodiments of the present invention, although the present invention is in no way restricted to the examples presented below.

A characteristic of the present invention is the use of a resin comprising a structural unit (a1) derived from a (meth)acrylate ester represented by the general formula (I) shown above as the aforementioned component (A).

The reason why the present invention enables a resist pattern to be formed with good control of the pattern size is not entirely clear, although the following are considered possible reasons. Namely, during resist pattern formation, light can leak marginally into the unexposed sections at the edges of the exposed sections, and although these edge sections do not become soluble in the developing liquid, a portion of the dissolution inhibiting groups within these regions may dissociate. In recent years, halftone phase shift masks have become widely used, particularly in those cases where hole patterns are formed, in order to deal with ever finer resist patterns, and light leakage is more likely in these types of cases.

At the same time, the base resins of ArF resists use bulky groups such as adamantyl skeletons containing a tertiary carbon atom as dissolution inhibiting groups.

reduced increases, and the range of such Tg reductions widens. As a result, in the case of a hole pattern for example, the greater the exposure becomes, the more likely it is that the resist will soften. Furthermore, it is surmised that the larger the pitch (the distance between patterns) becomes, the greater the volume of resist will be between adjacent patterns, meaning the quantity of resist flowing into the hole patterns will increase, causing an increased degree of narrowing of the hole patterns.

In contrast, it is thought that in the case of a resin of the present invention, because the resin must contain the structural unit (a1) described above, and utilizes non-bulky groups as the acid dissociable, dissolution inhibiting groups, the variation in the Tg value on dissociation of a dissolution inhibiting group is minimal, meaning the degree of narrowing can be maintained at an essentially uniform level.

<<Method of Forming a Resist Pattern>>

A method of forming a resist pattern according to the present invention utilizes a positive resist composition of the present invention, comprising a resin with a specific structural unit as a resin component (A) that displays increased alkali solubility under the action of acid, and an acid generator component (B) that generates acid on exposure, and comprises the following steps.

<Resist Pattern Formation Step>

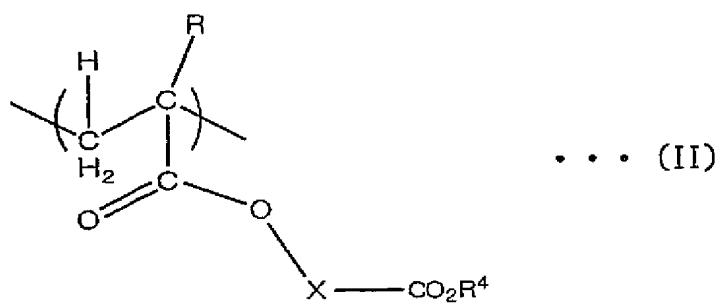
The resist pattern formation step can be conducted using a conventional resist pattern formation method, such as the method described below. Namely, a positive type resist composition such as that described below is first applied to the surface of a substrate such as a silicon wafer using a spinner or the like, and a prebake is conducted under temperature conditions of 80 to 150°C for 40 to 120 seconds, and preferably for 60 to 90 seconds, thereby forming a resist film. Following selective exposure of the resist film with an ArF excimer laser through a desired mask pattern using, for example, an ArF

The present invention utilizes a positive resist composition, which contains, as the aforementioned component (A), a resin that contains at least a structural unit (a1) derived from a (meth)acrylate ester represented by the general formula (I) shown above.

- Component (A)

[Structural unit (a1)]

The structural unit (a1) can be represented by a general formula (II) shown below.



(wherein, R^4 is a group comprising groups R^1 to R^3 and a carbon atom bonded thereto (namely, $-C(-R^1)(-R^2)-R^3$), and R, X, and R^1 to R^3 are as described below.)

The structural unit (a1) is a unit derived from a (meth)acrylate ester, in which the carboxyl group of the (meth)acrylic acid is bonded to the group X through an ester linkage, and the group R^4 is bonded, via an ester linkage, to a carboxyl group bonded to a ring within the group X.

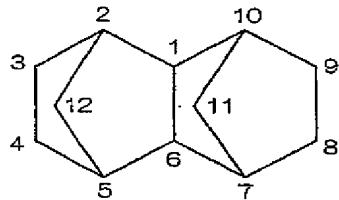
In the structural unit (a1), the group R^4 is an acid dissociable, dissolution inhibiting group, which displays an alkali dissolution inhibiting effect that causes the entire component (A) to be alkali insoluble prior to exposure, but dissociates under the action of acid generated from the acid generator following exposure, causing the entire component (A) to become alkali soluble.

Specific examples include groups in which 2 hydrogen atoms have been removed from a polycycloalkane such as adamantane, norbornane, isobornane, tricyclodecane or tetracyclododecane.

Of these, groups in which 2 hydrogen atoms have been removed from adamantane, groups in which 2 hydrogen atoms have been removed from norbornane, and groups in which 2 hydrogen atoms have been removed from tetracyclododecane are preferred from an industrial viewpoint.

Furthermore, the carboxyl group residues of the $-\text{CO}_2\text{R}^4$ group and the (meth)acrylate structural unit may be bonded to any position on the rings of the group X, as shown in the following formulas.

For example, in the case in which X is a group in which 2 hydrogen atoms have been removed from tetracyclododecane, the $-\text{CO}_2\text{R}^4$ group may be bonded to position 3 or 4 within the tetracyclododecane skeleton represented by the general formula shown below.



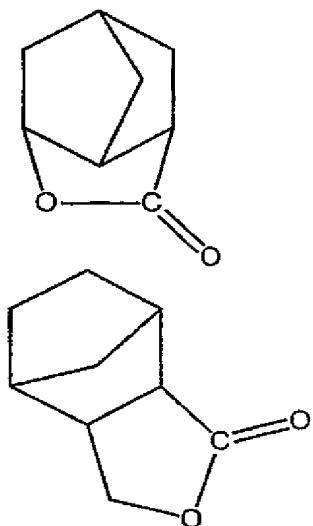
However, these bonding positions result in a mixture of stereoisomers, and so the bonding position cannot be specified. Similarly, the carboxyl group residue of the (meth)acrylate structural unit may be bonded to either position 8 or 9, although the position cannot be specified.

Furthermore, in the case in which X is a group in which 2 hydrogen atoms have been removed from adamantane, the $-\text{CO}_2\text{R}^4$ group may be bonded to position 1 or 2 within the adamantane skeleton represented by the general formula shown below.

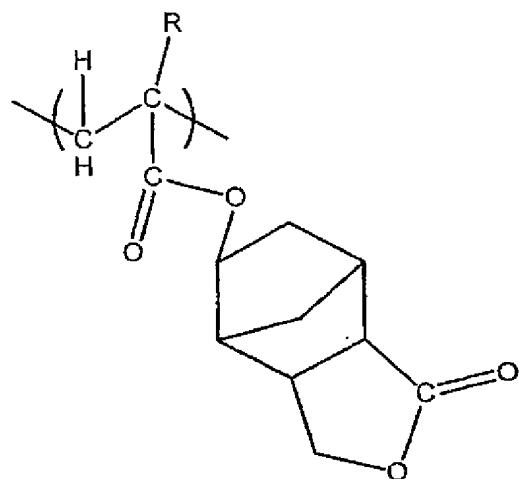
component (A) is used as a positive resist composition, the structural unit (a2) is effective in increasing the adhesion between the resist film and the substrate, and improving the affinity with the developing liquid.

There are no particular restrictions on the structural unit (a2), provided it contains this type of lactone unit.

Examples of the lactone unit include groups in which one hydrogen atom has been removed from the lactones shown in the structural formulas below.

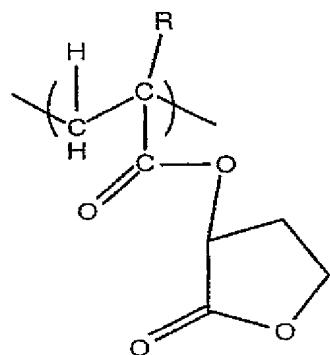


Furthermore in the structural unit (a2), the lactone unit is preferably at least one unit selected from a group consisting of compounds of the general formula (III) and the general formula (IV) shown below.



(wherein, R is a hydrogen atom or a methyl group)

[Formula 11]



(wherein, R is a hydrogen atom or a methyl group)

[Formula 12]

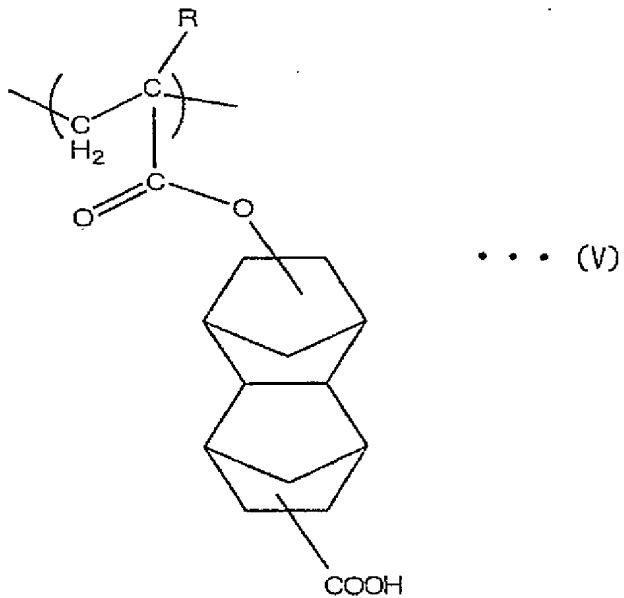
The structural unit (a3) can be appropriately selected from the multitude of ArF excimer laser resist composition resins that have been proposed, and polycyclic groups containing hydroxyl groups are preferred.

Suitable examples of the polycyclic group include the various groups listed as suitable examples of the group X in the above description for the structural unit (a1).

Specifically, preferred examples of the structural unit (a3) include hydroxyl group containing adamantyl groups (in which the number of hydroxyl groups is preferably from 1 to 3, and most preferably 1), and carboxyl group containing tetracyclododecanyl groups (in which the number of carboxyl groups is from 1 to 2, and most preferably 1).

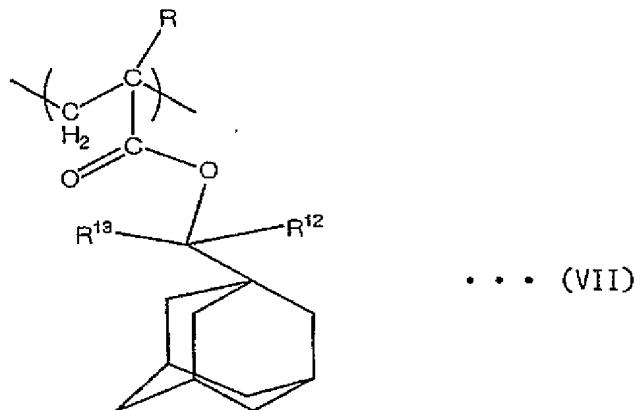
Carboxyl group containing tetracyclododecanyl groups are particularly preferred.

Specifically, if the structural unit (a3) has a structure represented by a general formula (V) shown below, then the dry etching resistance improves, as does the verticalness of the pattern cross-section, both of which are desirable.



(wherein, R represents a hydrogen atom or a methyl group)

(wherein, R represents a hydrogen atom or a methyl group, and R¹¹ represents a lower alkyl group)



(wherein, R represents a hydrogen atom or a methyl group, and R¹² and R¹³ each represent, independently, a lower alkyl group)

The structural unit represented by the general formula (VI) is a (meth)acrylate structural unit with a hydrocarbon group bonded through an ester linkage, and by bonding a straight chain or a branched alkyl group to the carbon atom of the adamantyl group that is adjacent to the oxygen atom (-O-) of the ester function, a tertiary alkyl group is formed within the ring skeleton of the adamantyl group.

Within the above formula, the group R¹¹ is preferably a straight chain or branched alkyl group of 1 to 5 carbon atoms, and specific examples include a methyl group, ethyl group, propyl group, isopropyl group, n-butyl group, isobutyl group, tert-butyl group, pentyl group, isopentyl group and neopentyl group. Of these, an alkyl group of at least 2 carbon atoms, and preferably 2 to 5 carbon atoms is preferred, and in such cases, the acid dissociability tends to increase compared with the case in which R¹¹ is a methyl group.

In terms of industrial availability, a methyl group is the most desirable.

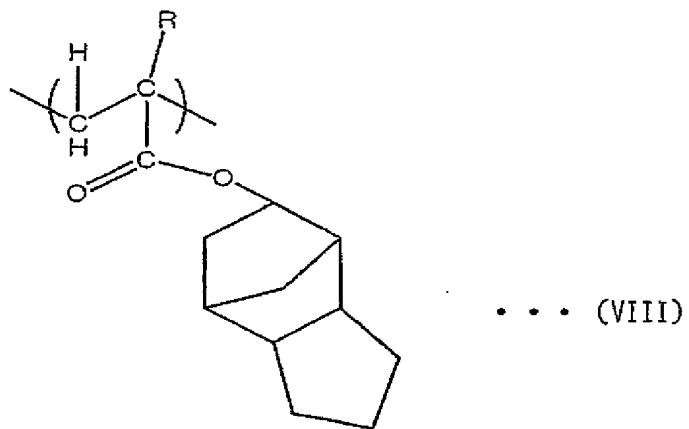
The (meth)acrylate structural unit represented by the aforementioned general formula (VII), like the general formula (VI), is a (meth)acrylate structural unit with a

are preferred. If this type of structural unit is used, then when the component (A) is used for a resist composition, the resolution for isolated patterns through to semi dense patterns (line and space patterns in which for a line width of 1, the space width is within a range from 1.2 to 2) is excellent, and consequently preferred.

Examples of the polycyclic group include the various groups listed as suitable examples of the group X in the above description for the structural unit (a1), and any of the multitude of materials conventionally used within ArF positive resist materials or KrF positive resist materials can be used.

From the viewpoint of industrial availability, at least one of a tricyclodecanyl group, an adamantyl group or a tetracyclododecanyl group are preferred.

Specific examples of the structural unit (a5) include the structures represented by the general formulas (VIII) to (X) shown below.



(wherein, R represents a hydrogen atom or a methyl group)

and an optional structural unit (a4), together with the structural unit (a2), the structural units with acid dissociable, dissolution inhibiting groups typically account for 20 to 70 mol%, and preferably from 40 to 60 mol% of the total of all the structural units, and the structural unit (a2) accounts for 30 to 80 mol%, and preferably from 40 to 60 mol%.

Furthermore, in the case of a polymer which in addition to the above components also contains the structural unit (a3), the structural units with acid dissociable, dissolution inhibiting groups typically account for 20 to 70 mol%, and preferably from 40 to 60 mol% of the total of all the structural units, the structural unit (a2) accounts for 20 to 60 mol%, and preferably from 30 to 50 mol%, and the structural unit (a3) account for 1 to 20 mol%, and preferably from 5 to 15 mol% of the total of all the structural units.

The component (A) comprises a structural unit (a1^a) derived from an acrylate ester and/or a structural unit (a1^m) derived from a methacrylate ester as the structural unit (a1).

Similarly, the other structural units (a2), (a3), (a4) and (a5) also comprise structural units derived from acrylic acid and/or methacrylic acid.

There are no particular restrictions on the weight average molecular weight (Mw) (polystyrene equivalent) of the component (A), although values within a range from 4,000 to 30,000 are preferred, and values from 7,000 to 15,000 are even more desirable. If the molecular weight is greater than this range, then there is a danger of a deterioration in the solubility of the component in the resist solvent, whereas if the molecular weight is too small, there is a danger of a deterioration in the cross sectional shape of the resist pattern.

Furthermore, there are no particular restrictions on the value of Mw/(number average molecular weight (Mn)), although values within a range from 1.0 to 6.0 are preferred, and values from 1.5 to 2.5 are even more desirable. If the value is greater than this range, the resolution and the pattern shape tend to deteriorate.

A resist composition of the present invention is produced by dissolving the component (A) and the component (B), together with an optional component described below, preferably in an organic solvent.

The organic solvent can be any solvent capable of dissolving the component (A) and the component (B) to generate a uniform solution, and the solvent used can be one, or two or more solvents selected from amongst known solvents used for conventional chemically amplified resists.

Specific examples of the solvent include ketones such as acetone, methyl ethyl ketone, cyclohexanone, methyl isoamyl ketone and 2-heptanone; polyhydric alcohols and derivatives thereof such as ethylene glycol, ethylene glycol monoacetate, diethylene glycol, diethylene glycol monoacetate, propylene glycol, propylene glycol monoacetate, dipropylene glycol, or the monomethyl ether, monoethyl ether, monopropyl ether, monobutyl ether or monophenyl ether of dipropylene glycol monoacetate; cyclic ethers such as dioxane; and esters such as methyl lactate, ethyl lactate, methyl acetate, ethyl acetate, butyl acetate, methyl pyruvate, ethyl pyruvate, methyl methoxypropionate, and ethyl ethoxypropionate. These organic solvents can be used singularly, or as a mixed solvent of two or more different solvents.

In particular, mixed solvents of propylene glycol monomethyl ether acetate (PGMEA) and a polar solvent containing a hydroxyl group or a lactone such as propylene glycol monomethyl ether (PGME), ethyl lactate (EL) or γ -butyrolactone offer good improvement in the storage stability of the positive resist composition, and are consequently preferred.

In those cases where EL is added, the weight ratio of PGMEA:EL is preferably within a range from 6:4 to 4:6.

These types of amines are typically added in quantities within a range from 0.01 to 1.0% by weight relative to the quantity of the component (A).

Miscible additives can also be added to a positive resist composition of the present invention according to need, including additive resins for improving the properties of the resist film, surfactants for improving the ease of application, dissolution inhibitors, plasticizers, stabilizers, colorants and halation prevention agents.

In terms of the light source used in the exposure process, although a positive resist composition of the present invention is particularly applicable to ArF excimer lasers, it is also effective for other types of radiation, including radiation of longer wavelength such as KrF excimer lasers, and radiation of shorter wavelength such as F₂ excimer lasers, EUV (extreme ultraviolet radiation), VUV (vacuum ultraviolet radiation), electron beams, X-rays and soft X-rays.

<Narrowing Step>

In the present invention, the narrowing step is performed following development of the resist pattern, in order to narrow the pattern size of the resist pattern.

- Thermal Flow Process

One method that can be favorably used for the narrowing step is a method known as a thermal flow process.

A thermal flow process can be carried out in the manner described below. Namely, the developed resist pattern is heated at least once, and preferably 2 to 3 times, to soften the resist, and by causing the resist to flow, the pattern size of the resist pattern (such as the hole diameter within a hole pattern or the space width within a line and space pattern) is shrunk to a smaller value than that immediately following developing.

dialkylene glycol or trialkylene glycol, or a polyhydric alcohol such as trimethylolpropane, pentaerythritol or pentaglycol have been substituted with vinyl ethers.

Specific examples of such compounds include ethylene glycol divinyl ether, diethylene glycol divinyl ether, triethylene glycol divinyl ether, 1,4-butanediol divinyl ether, tetramethylene glycol divinyl ether, tetraethylene glycol divinyl ether, neopentyl glycol divinyl ether, trimethylolpropane trivinyl ether, trimethylolethane trivinyl ether, hexanediol divinyl ether, 1,4-cyclohexanediol divinyl ether, tetraethylene glycol divinyl ether, pentaerythritol divinyl ether, pentaerythritol trivinyl ether, and cyclohexanedimethanol divinyl ether. Of these, divinyl ethers of alkylene glycols with an alicyclic group such as cyclohexanedimethanol divinyl ether are particularly preferred.

This cross linking compound with at least two vinyl ether groups of the component (C) is typically added at a rate of 0.1 to 25 parts by weight, and preferably from 1 to 15 parts by weight, per 100 parts by weight of the component (A). The component (C) may utilize either a single compound, or a mixture of two or more different compounds.

- Shrink Process

Another example of an ideal process for the narrowing step is the shrink process that has been proposed by the applicants of the present invention.

In this shrink process, a resist pattern formed on a substrate is coated with a water soluble resin coating, and this water soluble resin coating is shrunk by subsequent heat treatment, and this heat shrinkage action is used to narrow the spacing in the resist pattern.

More specifically, first a coating formation agent comprising a water soluble polymer is applied to the surface of a resist pattern formed on a substrate, preferably forming a layered product in which the water soluble resin coating covers the entire

treatment of the substrate. The softening point of the resist pattern varies depending on the resist composition used to form the resist pattern. Taking into consideration the softening points of the various resist compositions used in current lithography techniques, a preferred heat treatment is typically conducted at a temperature within a range from 80 to 160°C, at a temperature that does not cause fluidization of the resist, for a period of 30 to 90 seconds.

The thickness of the water soluble resin coating is preferably either approximately equal to the height of the photoresist pattern, or of a height sufficient to cover the resist pattern, and is typically within a range from 0.1 to 0.5 µm.

Subsequently, the heat shrunk water soluble resin coating, which still remains on the pattern, is removed by washing with an aqueous solvent, and preferably with pure water, for 10 to 60 seconds. The water soluble resin coating is easily removed by washing with water, and is able to be completely removed from the substrate and the resist pattern.

There are no particular restrictions on the water soluble polymer contained within the coating formation agent used to form the water soluble resin coating, provided the polymer is soluble in water at room temperature, although resins comprising structural units derived from at least one monomer which acts as a proton donor, and structural units derived from at least one monomer which acts as a proton acceptor are ideal. By using this type of resin, volumetric shrinkage can be favorably carried out by heating.

This type of water soluble polymer may also be a copolymer comprising structural units derived from at least one monomer which acts as a proton donor, and structural units derived from at least one monomer which acts as a proton acceptor, or a mixture of a polymer with structural units derived from at least one monomer which acts as a proton donor, and a polymer with structural units derived from at least one monomer

Specific examples of suitable urea polymers include polymers formed from monomer components such as methylolated urea, dimethylolated urea, and ethylene urea.

Specific examples of suitable melamine polymers include polymers formed from monomer components such as methoxymethylated melamine, methoxymethylated isobutoxymethylated melamine, and methoxyethylated melamine.

In addition, water soluble epoxy based polymers and nylon based polymers can also be used.

Of the above polymers, a composition comprising at least one polymer selected from a group consisting of alkylene glycol based polymers, cellulose based polymers, vinyl based polymers and acrylic based polymers is preferred, and acrylic resins are the most preferred as they also offer simple pH adjustment. In addition, using a copolymer of an acrylic based monomer, and another non-acrylic monomer capable of forming a water soluble polymer is preferred, as such copolymers enable efficient narrowing of the photoresist pattern size, while maintaining the shape of the photoresist pattern during the heat treatment. The water soluble polymer may be either a single polymer, or a mixture of two or more polymers.

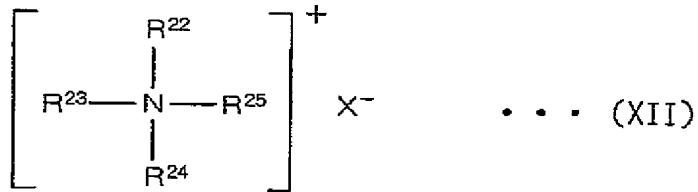
The monomer which acts as a proton donor is preferably acrylamide or N-vinylpyrrolidone.

The monomer which acts as a proton acceptor is preferably acrylic acid or the like.

A water soluble polymer comprising polymer structural units derived from N-vinylpyrrolidone as the proton donor monomer, and polymer structural units derived from acrylic acid as the proton acceptor monomer is particularly preferred.

Specific examples of such N-alkylpyrrolidone based surfactants include N-hexyl-2-pyrrolidone, N-heptyl-2-pyrrolidone, N-octyl-2-pyrrolidone, N-nonyl-2-pyrrolidone, N-decyl-2-pyrrolidone, N-undecyl-2-pyrrolidone, N-dodecyl-2-pyrrolidone, N-tridecyl-2-pyrrolidone, N-tetradecyl-2-pyrrolidone, N-pentadecyl-2-pyrrolidone, N-hexadecyl-2-pyrrolidone, N-heptadecyl-2-pyrrolidone, and N-octadecyl-2-pyrrolidone. Of these, N-octyl-2-pyrrolidone ("Surfadone LP100", manufactured by ISP Co., Ltd.) is preferred.

Amongst quaternary ammonium salt based surfactants, compounds represented by a general formula (XII) shown below are preferred.



(wherein, R²², R²³, R²⁴ and R²⁵ each represent, independently, an alkyl group or a hydroxyalkyl group (although at least one of the groups represents an alkyl group or a hydroxyalkyl group of 6 or more carbon atoms); and X⁻ represents a hydroxide ion or a halogen ion)

Specific examples of such quaternary ammonium salt based surfactants include dodecyltrimethylammonium hydroxide, tridecyltrimethylammonium hydroxide, tetradecyltrimethylammonium hydroxide, pentadecyltrimethylammonium hydroxide, hexadecyltrimethylammonium hydroxide, heptadecyltrimethylammonium hydroxide, and octadecyltrimethylammonium hydroxide. Of these, hexadecyltrimethylammonium hydroxide is preferred.

N,N-diethylethanolamine, N,N-dibutylethanolamine, N-methylethanolamine, N-ethylmethanolamine, N-butylethanolamine, N-methyldiethanolamine, monoisopropanolamine, diisopropanolamine, and triisopropanolamine; polyalkylene polyamines such as diethylenetriamine, triethylenetetramine, propylenediamine, N,N-diethylenediamine, 1,4-butanediamine, N-ethyl-ethylenediamine, 1,2-propanediamine, 1,3-propanediamine, and 1,6-hexanediamine; aliphatic amines such as 2-ethyl-hexylamine, dioctylamine, tributylamine, tripropylamine, triallylamine, heptylamine, and cyclohexylamine; aromatic amines such as benzylamine and diphenylamine; and cyclic amines such as piperazine, N-methyl-piperazine, methyl-piperazine, and hydroxyethylpiperazine. Of these, amines with boiling points of 140°C (760 mmHg) or higher are preferred, and monoethanolamine and triethanolamine are particularly preferred.

In those cases in which a water soluble amine is added, the quantity of the amine is preferably within a range from 0.1 to 30% by weight, and even more preferably from 2 to 15% by weight, relative to the total solid fraction of the coating formation agent. If the quantity is less than 0.1% by weight then there is a danger of a deterioration of the solution over time, whereas in contrast, if the quantity exceeds 30% by weight, there is a danger of a deterioration in the shape of the photoresist pattern.

From the viewpoints of reducing the photoresist pattern size and suppressing the occurrence of defects, an additional non-amine based water soluble organic solvent may also be added if desired.

This non-amine based water soluble organic solvent may be any non-amine based organic solvent that displays miscibility with water, and suitable examples include sulfoxides such as dimethylsulfoxide; sulfones such as dimethyl sulfone, diethyl sulfone, bis(2-hydroxyethyl) sulfone, and tetramethylene sulfone; amides such as

does increasing the concentration not produce an equivalent improvement in the desired effects, but the handling of the agent also becomes more difficult.

As described above, the coating formation agent is usually used in the form of an aqueous solution using water as the solvent, although a mixed solvent of water and an alcohol based solvent could also be used. Examples of this alcohol based solvent include monovalent alcohols such as methyl alcohol, ethyl alcohol, propyl alcohol, and isopropyl alcohol. The alcohol based solvent is added to the water in quantities of no more than 30% by weight.

EXAMPLES

As follows is a more detailed description of the present invention based on a series of examples, although the present invention is in no way restricted to the examples presented below. Unless otherwise stated, quantities refer to weight % values.

[Example 1]

0.1 mol of a compound represented by a formula 22 shown below, 0.08 mol of the norbornane lactone acrylate of the formula 9, and 0.02 mol of a compound represented by a formula 23 shown below were dissolved in 500 ml of methyl ethyl ketone (MEK), and 0.1 mol of AIBN was then added to the solution and dissolved. The thus obtained solution was heated to a temperature of 65 to 70°C, and this temperature was maintained for 3 hours. Subsequently, the reaction solution was poured into 3 L of vigorously stirred isopropanol, and the precipitated solid was isolated by filtration. The thus obtained solid product was dissolved in 300 ml of MEK, poured into 3 L of vigorously stirred methanol, and once again the precipitated solid was isolated by filtration and then dried, and yielded

weight of triethanolamine, and 750 parts by weight of a mixed solvent of PGMEA:EL (6:4), and following dissolution, the solution was filtered through a filter of pore size 0.45 μ m, thereby completing preparation of a positive resist composition.

The thus obtained positive resist composition was applied to a silicon wafer using a spinner, and was then prebaked and dried on a hotplate at 115°C for 90 seconds, thereby forming a resist layer with a film thickness of 300 nm.

This layer was then selectively irradiated with an ArF excimer laser (193 nm) through a mask pattern, using an ArF exposure apparatus NSR-S302 (manufactured by Nikon Corporation; NA (numerical aperture) = 0.60; σ = 0.75).

The resist was then subjected to PEB treatment at 115°C for 90 seconds, subsequently subjected to puddle development for 30 seconds at 23°C in a 2.38% by weight aqueous solution of tetramethylammonium hydroxide, and was then washed for 20 seconds with water, and dried.

As a result of this photoresist pattern formation process, a hole pattern (including a 1:1 dense pattern and a 1:3 isolated pattern) with a hole diameter of 140 nm was formed.

Next, a water soluble resin coating with a total solid fraction concentration of 8.0% by weight, which was formed by dissolving 10 g of a copolymer of acrylic acid and vinylpyrrolidone (acrylic acid : vinylpyrrolidone = 2:1 (weight ratio)), and 0.02 g of "Surfadone LP100" (manufactured by ISP Co., Ltd.) as an N-alkylpyrrolidone based surfactant in pure water, was applied to the surface of the hole pattern to form a layered product. The film thickness (the height from the surface of the substrate) of the water soluble resin coating of the layered product was 200 nm. The layered product was then subjected to heat treatment for 60 seconds at a temperature of 110°C, 120°C, 130°C, or 140°C. Subsequently, the water soluble resin coating was removed by washing with pure water at 23°C.

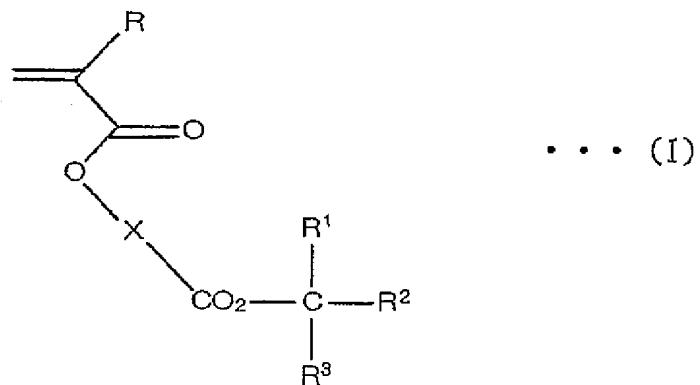
differences in the exposure dose or the pitch also caused large differences in the degree of narrowing, and even comparing values at the same temperature and the same exposure dose, the isolated pattern displayed a larger degree of narrowing than the dense pattern.

INDUSTRIAL APPLICABILITY

According to the present invention, a resist pattern with minimal pattern variation within the plane of the substrate, and excellent uniformity can be formed with good control of the pattern size, which is industrially very useful.

2. A method of forming a resist pattern according to claim 1, wherein said component (A) utilizes a resin with a structural unit (a1) in which said groups R¹ to R³ each represent, independently, a lower alkyl group.
3. A method of forming a resist pattern according to claim 2, wherein said component (A) utilizes a resin with a structural unit (a1) in which said lower alkyl groups are either methyl groups or ethyl groups.
4. A method of forming a resist pattern according to claim 1, wherein said component (A) utilizes a resin further comprising a structural unit (a2) derived from a (meth)acrylate ester with a lactone unit.
5. A method of forming a resist pattern according to claim 1, wherein said component (B) utilizes an onium salt with a fluorinated alkylsulfonate ion as an anion.
6. A method of forming a resist pattern according to claim 1, wherein said positive resist composition further comprises a secondary or a tertiary lower aliphatic amine.
7. A method of forming a resist pattern according to claim 1, wherein said narrowing step is a thermal flow process in which said resist pattern is heated and softened, and a pattern size of said resist pattern is narrowed.
8. A method of forming a resist pattern according to claim 7, wherein said positive resist composition further comprises a compound with at least two vinyl ether groups, which reacts with said resin component (A) on heating and forms cross linking.

said component (A) is a resin with a structural unit (a1) derived from a (meth)acrylate ester represented by a general formula (I) shown below:



wherein, R represents a hydrogen atom or a methyl group; X represents a hydrocarbon group with 1 to 4 rings; R¹ to R³ either each represent, independently, a lower alkyl group, or alternatively, one of R¹ to R³ represents a lower alkyl group, and two remaining groups represent lower alkylene groups, terminals of which are bonded together to form a single ring containing 5 or 6 carbon atoms including bonded terminal carbon atoms.

14. A layered product in which a resist layer formed from a positive resist composition according to claim 13, and a water soluble resin coating comprising a water soluble polymer on the resist layer are layered onto a substrate.

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FIG. 2A

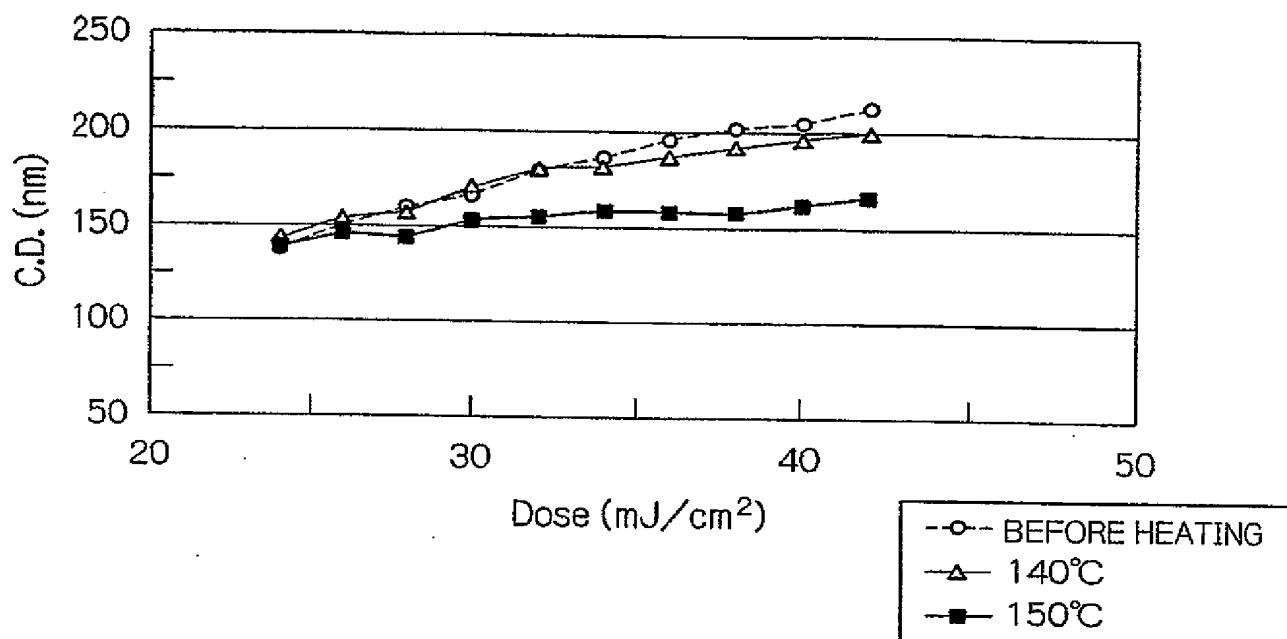
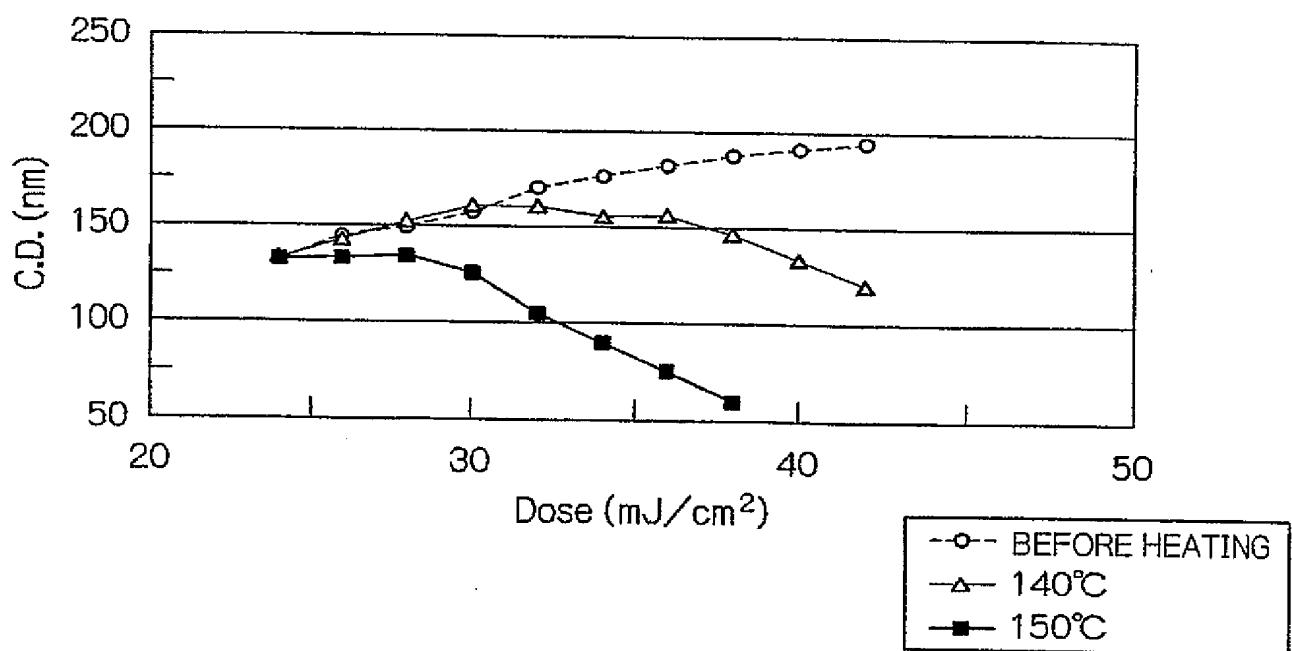


FIG. 2B



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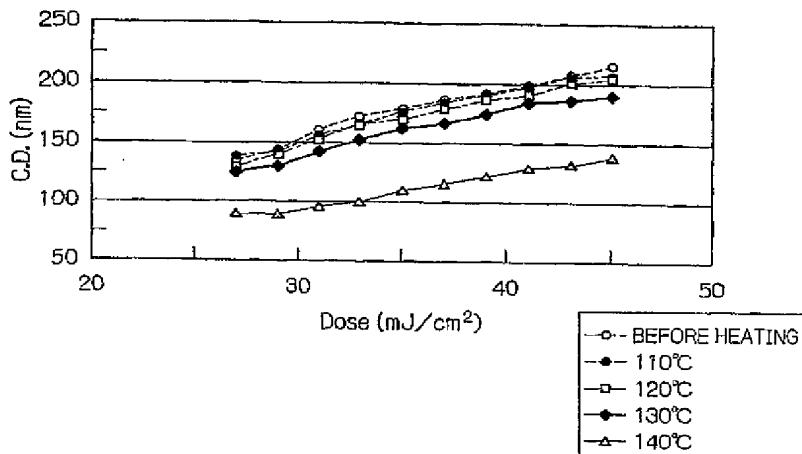
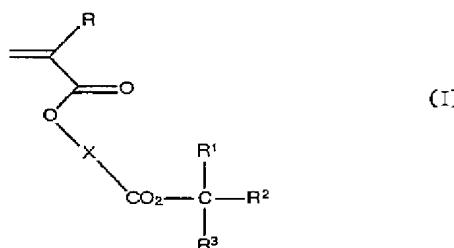
(74) Agents: TANAI, Sumio et al.; 2-3-1, Yaesu, Chuo-ku, Tokyo 104-8453 (JP).

(81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, KE, KG, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

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[Continued on next page]

(54) Title: METHOD OF FORMING RESIST PATTERN, POSITIVE RESIST COMPOSITION, AND LAYERED PRODUCT



(57) Abstract: There are provided a method of forming a resist pattern that enables the resist pattern to be formed with good control of the pattern size, as well as a positive resist composition used in the method, and a layered product formed using the positive resist composition. In the above method a positive resist composition comprising a resin component (A), which contains a structural unit (a1) derived from a (meth)acrylate ester represented by a general formula (I) shown below, and displays increased alkali solubility under action of acid, and an acid generator component (B) that generates acid on exposure is applied to a substrate, a prebake is conducted, the resist composition is selectively exposed, post exposure baking (PEB) is conducted, alkali developing is then used to form a resist pattern, and the pattern size of the thus produced resist pattern is then narrowed by heat treatment.

INTERNATIONAL SEARCH REPORT

International Application No

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A. CLASSIFICATION OF SUBJECT MATTER
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According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 1 260 864 A (FUJI PHOTO FILM CO., LTD) 27 November 2002 (2002-11-27) examples 208,218	13
X	JP 2000 330287 A (TOSHIBA CORP) 30 November 2000 (2000-11-30) examples 6,7	13
X	PATENT ABSTRACTS OF JAPAN vol. 2002, no. 06, 4 June 2002 (2002-06-04) & JP 2002 040661 A (TORAY IND INC), 6 February 2002 (2002-02-06) abstract	13
X	US 2001/026901 A1 (MAEDA KATSUMI ET AL) 4 October 2001 (2001-10-04) example 29	13
		-/-

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Date of the actual completion of the international search	Date of mailing of the international search report
25 July 2005	29/07/2005
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer Rández García, J

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/JP 03/15347

Patent document cited in search report		Publication date		Patent family member(s)		Publication date
EP 1260864	A	27-11-2002	JP	2002351077 A	04-12-2002	
			JP	2002351079 A	04-12-2002	
			JP	2002351063 A	04-12-2002	
			DE	60200970 D1	23-09-2004	
			EP	1260864 A1	27-11-2002	
			US	2003077540 A1	24-04-2003	
JP 2000330287	A	30-11-2000		NONE		
JP 2002040661	A	06-02-2002		NONE		
US 2001026901	A1	04-10-2001	JP	3042618 B2	15-05-2000	
			JP	2000026446 A	25-01-2000	
			JP	3166848 B2	14-05-2001	
			JP	2000147769 A	26-05-2000	
			WO	0001684 A1	13-01-2000	
WO 03048861	A	12-06-2003	JP	2003241385 A	27-08-2003	
			AU	2002354248 A1	17-06-2003	
			CN	1592870 A	09-03-2005	
			EP	1452917 A1	01-09-2004	
			WO	03048861 A1	12-06-2003	
			JP	2005128572 A	19-05-2005	
			JP	2005128573 A	19-05-2005	
			TW	573230 B	21-01-2004	
			US	2005095535 A1	05-05-2005	
			US	2004110085 A1	10-06-2004	
US 2004110085	A1	10-06-2004	JP	2003241385 A	27-08-2003	
			AU	2002354248 A1	17-06-2003	
			CN	1592870 A	09-03-2005	
			EP	1452917 A1	01-09-2004	
			WO	03048861 A1	12-06-2003	
			JP	2005128572 A	19-05-2005	
			JP	2005128573 A	19-05-2005	
			TW	573230 B	21-01-2004	
			US	2005095535 A1	05-05-2005	
WO 03048863	A	12-06-2003	JP	2003167347 A	13-06-2003	
			AU	2002354273 A1	17-06-2003	
			CN	1578931 A	09-02-2005	
			EP	1452919 A1	01-09-2004	
			WO	03048863 A1	12-06-2003	
			US	2004058269 A1	25-03-2004	
US 2004058269	A1	25-03-2004	JP	2003167347 A	13-06-2003	
			AU	2002354273 A1	17-06-2003	
			CN	1578931 A	09-02-2005	
			EP	1452919 A1	01-09-2004	
			WO	03048863 A1	12-06-2003	
EP 1273974	A	08-01-2003	JP	2003107752 A	09-04-2003	
			JP	3578403 B2	20-10-2004	
			JP	2003084448 A	19-03-2003	
			JP	3662870 B2	22-06-2005	
			JP	2003084459 A	19-03-2003	
			JP	3628010 B2	09-03-2005	
			JP	2003084460 A	19-03-2003	